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A NEW REDUCTION SYSTEM: COMBINATION OF SODIUM SULFIDE (SODIUM HYDROSULFIDE) WITH PHASE TRANSFER AGENT IN A TWO-PHASE MIXTURE. REDUCTIVE DEBROMINATION OF *vic*-DIBROMIDES TO OLEFINS

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Abstract: A wide variety of *vic*-dibromides are debrominated to the corresponding olefins in good to excellent yields by aqueous sodium sulfide or sodium hydrosulfide using trioctylmethylammonium chloride as the phase transfer agent in a two-phase mixture.

It has long been known that S^{2-} and HS^- function as reducing agent. Although sodium sulfide and sodium hydrosulfide are most inexpensive chemicals, their use as reducing agent is rather limited.[1] This is probably due to their strong nucleophilicity toward electrophiles (therefore, nucleophilic substitution often predominates over process leading to reduction products) and also due to their insolubility in ordinary organic solvents. In the belief that their maximal ability as reducing agent might be displayed by solubilizing them in nonpolar aprotic solvents, thus overcoming the latter shortage, we examined the use of these reagents in a combination with phase transfer agents in a two-phase mixture. As a result, we found that the combination of these reagents with trioctylmethylammonium chloride constitutes a strong reduction system. As a primary application of this system to organic synthesis, we report here the reductive debromination of *vic*-dibromides to olefins, which is one of fundamental conversions in organic chemistry.[2-4]

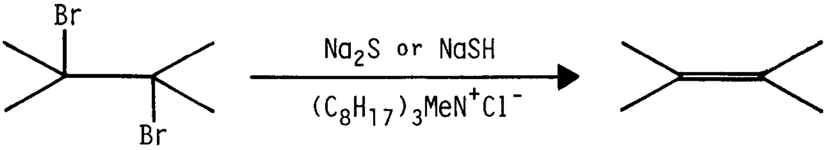
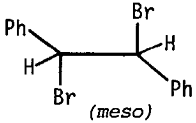
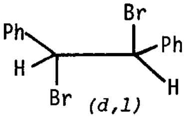
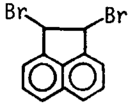
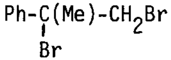
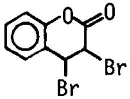
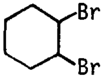
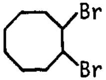
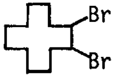
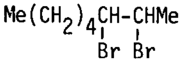
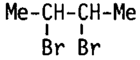
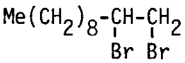
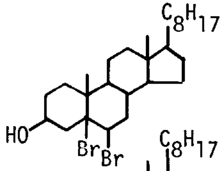
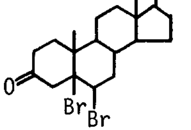
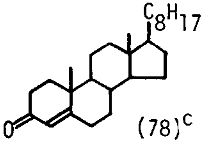
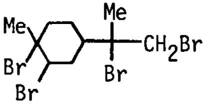
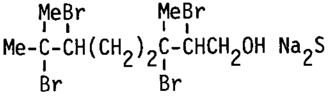
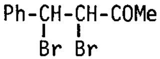


Table summarizes the yields of olefins from a series of *vic*-dibromides under a two-phase catalytic conditions. The advantages from a synthetic point of view and characteristic features of the present method are as follows:

1) Sodium sulfide nonahydrate and sodium hydrosulfide hydrate are reagents inexpensive and easy to handle. Trioctylmethylammonium chloride is commercially available from various sources at a reasonable price.

2) The reaction can be done by simply stirring a two-phase mixture for a short period at

Table Reductive Debromination of *vic*-Dibromides to Olefins[a]

Entry	*vic*-Dibromides	Reducing Reagent	Organic Solvent	Time (h)	Olefins (Yield, %)[b]
1	 (*meso*)	Na_2S	Benzene	1	trans-Stilbene (93)
2	As above	NaSH	Benzene	1	trans-Stilbene (94)
3	 (*d,l*)	Na_2S	Benzene	1	Stilbene (96) cis:trans=87:13
4	As above	NaSH	Benzene	1	Stilbene (97) cis:trans=85:15
5		Na_2S	Benzene	1	Acenaphthylene (92)
6	 $Ph\text{-}\underset{Br}{C}(Me)\text{-}CH_2Br$	Na_2S	Pentane	0.5	α-Methylstyrene (73)
7		Na_2S	Benzene	1	Coumarin (88)
8		Na_2S	None	2	Cyclohexene (90)
9		Na_2S	None	2	Cyclooctene (60)
10		Na_2S	None	2	Cyclododecene (72)
11	 $Me(CH_2)_4\underset{Br}{CH}\text{-}\underset{Br}{CH}Me$	Na_2S	None	2	2-Octene (80)
12	 $Me\text{-}\underset{Br}{CH}\text{-}\underset{Br}{CH}\text{-}Me$	Na_2S	None	0.5	2-Butene (60)
13	As above	NaSH	None	0.5	2-Butene (70)
14	 $Me(CH_2)_8\text{-}\underset{Br}{CH}\text{-}\underset{Br}{CH_2}$	Na_2S	Hexane	1	1-Undecene (12)
15		Na_2S	Benzene	1	Cholesterol (86)
16		Na_2S	Benzene	1	 (78)[c]
17		Na_2S	Benzene	1	Limonene (41)
18	 $Me\text{-}\overset{Me\,Br}{\underset{Br}{C}}\text{-}CH(CH_2)_2\overset{Me\,Br}{\underset{Br}{C}}\text{-}CHCH_2OH$	Na_2S	Benzene	1	Geraniol (64)
19	 $Ph\text{-}\underset{Br}{CH}\text{-}\underset{Br}{CH}\text{-}COMe$	Na_2S	Benzene	1	Benzalacetone (84)

[a] In all of the cases, *vic*-dibromide, sodium sulfide nonahydrate (sodium hydrosulfide hydrate), and trioctylmethylammonium chloride were employed in a molar ratio of about 1:2.2:0.1.

[b] Yields based on isolated pure olefins.

[c] Under the conditions, primary product Δ^5-cholesten-3-one isomerized to Δ^4-cholesten-3-one.

room temperature. The following is typical.

To a stirred mixture of *meso*-1,2-dibromo-1,2-diphenylethane (5 mmol) and a catalytic amount of trioctylmethylammonium chloride (0.5 mmol) in benzene (10 mL) was added sodium sulfide nonahydrate (11 mmol) dissolved in water (10 mL) all at once (a mildly exothermic reaction occurs immediately with development of a deep coloration[5]). After stirring for 1 h, the benzene layer was washed with water, dried, and evaporated. The residue was passed through a short silica gel column with hexane as eluent to give *trans*-stilbene in 93% yield (Entry 1).

3) Since the reaction can be done without the use of organic solvent, even volatile olefins can be easily isolated in a pure form free from organic solvent and without mechanical loss (Entry 8-11) as exemplified below.

1,2-Dibromocyclohexane (70 mmol), trioctylmethylammonium chloride (5 mmol), and sodium sulfide nonahydrate (150 mmol) dissolved in a minimal amount of water (24 mL) were placed in a 200-mL separatory funnel. The funnel was mechanically shaken for 2 h. The lower aqueous layer was discarded, and the upper layer was washed with water, dried, and distilled to give pure cyclohexene in 90% yield (Entry 8).

By the same reason as described above, even a gaseous olefin at room temperature can be readily isolated (Entry 12 and 13). In this case, the olefin liberated is collected in a gas buret or in a trap cooled by a dry ice-acetone bath.

4) The reaction is not accompanied by reduction of other functional groups such as ester and carbonyl groups (Entry 7, 16, and 19), and therefore its application to structurally complex molecules is also possible without difficulty.

5) The debromination occurs in a stereospecific *anti*-elimination manner (Entry 1-4).

6) The only limitation is observed in Entry 14, in which the olefin is produced in a low yield. In this case, nucleophilic substitution predominates over reduction probably because of steric and electronic reasons (cf. Entry 6).[6]

7) Finally, debromination of a carboxylic acid such as *erythro*-2,3-dibromo-3-phenylpropionic acid can be achieved without the use of a phase transfer agent, because it is soluble in an aqueous sodium sulfide solution. A mixture of *erythro*-2,3-dibromo-3-phenylpropionic acid (10 mmol) and sodium sulfide nonahydrate (22 mmol) in water (60 mL) was stirred for 1 h at room temperature. Acidic workup of the mixture gave *trans*-cinnamic acid in 97% yield.

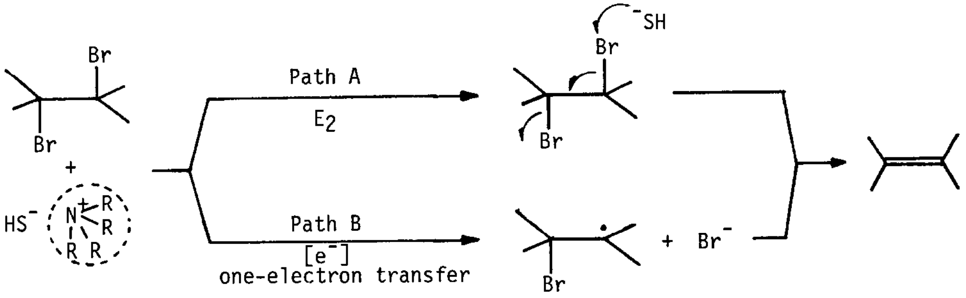
In summary, the method developed here for conversion of *vic*-dibromides to olefins[7] is far more convenient than any other reported methods in many respects.[3,8]

References and Notes

1. a) Reduction of aromatic nitro and related compounds; T. Ogata, "Sanka To Kangen," 2nd Ed., Nankodo, Tokyo, 1964, p. 879. b) Reduction of aliphatic dinitro compounds to olefins; N. Kornblum, S. D. Boyd, H. W. Pinnick, and R. G. Smith, *J. Am. Chem. Soc.*, **93**, 4316 (1971) [see also, N. Ono, R. Tamura, J. Hayami, and A. Kaji, *Tetrahedron Lett.*, 763 (1978)]. c) Reduction of alkenic nitro compounds; N. Ono, S. Kawai, K. Tanaka, and A. Kaji, *Tetrahedron Lett.*, 1733 (1979). d) Reduction of azides to amines; M. O. Forster

and K. N. Rao, *J. Chem. Soc.*, 1943 (1926). e) Reduction of *vic*-dibromides to olefins; K. Fukunaga and H. Yamaguchi, *Synthesis*, 879 (1981).

2. It was reported very recently that this conversion is effected by sodium sulfide in dimethylformamide as solvent.[1e]
3. For representative methods for this conversion, see a) reference 1e and a number of references cited therein; b) S. W. Bennett, C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Organometal. Chem.*, **27**, 195 (1971); c) T. -L. Ho and C. M. Wong, *Synth. Commun.*, **5**, 87 (1975); d) T. Kempe, T. Norin, and R. Caputo, *Acta. Chem. Scand. B*, **30**, 366 (1976); e) K. Ramasamy, S. K. Kalyanasundaram, and P. Shanmugam, *Synthesis*, 311 (1978); f) J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 2408 (1974); g) F. Sato, T. Akiyama, K. Iida, and M. Sato, *Synthesis*, 1025 (1982); h) D. Savoia, E. Tagliavini, C. Trombini, and A. Umani-Ronchi, *J. Org. Chem.*, **47**, 876 (1982).
4. Quaternary ammonium chlorides having short alkyl chains such as tetraethylammonium chloride cannot catalyze this conversion.
5. Color differs with cases. Generally mixture first turns dark red to brown, and then the color gradually fades to give the orange to red mixture finally.
6. Under a two-phase catalytic conditions, alkyl halides react with sodium sulfide to give dialkyl sulfides nearly quantitatively; C. M. Starks and C. Liotta, "Phase Transfer Catalysis," Academic Press, New York, 1978, p. 138.
7. The present method cannot be applied to dechloriation of *vic*-dichlorides, because dehydrochlorination occurs preferentially. Refluxing a mixture of *meso*-1,2-dichloro-1,2-diphenylethane (2 mmol), trioctylmethylammonium chloride (0.2 mmol), sodium sulfide nonahydrate (4.4 mmol), benzene (5 mL), and water (5 mL) for 6 h gave α-chloro-*cis*-stilbene (80%) and the starting dichloride (16%) (the reaction does not proceed at room temperature), while treatment of *d,l*-1,2-dichloro-1,2-diphenylethane under the same conditions for 2 h gave α-chloro-*trans*-stilbene in 98% yield.
8. In reduction with sodium sulfide, the actual species which participates in reaction must be HS^-, because S^{2-} is extensively hydrolyzed to HS^- in aqueous solutions (F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd Ed., Interscience, New York, 1967, p. 529), and also HS^- is far more easily transfered to organic phase than S^{2-}. Two plausible mechanisms will be then put forward; one involves an E_2 type elimination (path A), and the other involves a one-electron transfer process (path B).



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